

Colloid Chemistry of Layered Perovskite Niobate

Kenji Toda, Ken-ichi Shimizu, Hiroki Sato*, Akira Sugawara*, Kazuyoshi Uematsu*
and Mineo Sato*

Graduate School of Science and Technology, Niigata University, Ikarashi 2-nocho, Niigata, 950-2181

Fax: 81-25-262-6771, e-mail: ktoda@eng.niigata-u.ac.jp

*Faculty of Engineering, Niigata University, 8050 Ikarashi 2-no-cho, Niigata 950-2181

In this study, we report the reaction mechanism of well-crystalline nano-particles of potassium niobate KNbO_3 via a new colloid chemistry method at room temperature. Local structure of perovskite nano-sheet in the colloidal solution and nano-particles were investigated by Nb K-edge XAFS (XANES/EXAFS) spectroscopy. The crystal structure of nano-particles was determined by a Rietveld refinement of a neutron powder diffraction pattern. The XANES and EXAFS data indicate clear evidence that the nano-sheets consist of distorted Nb-O polyhedra with low coordination number.

Key words: Soft Chemistry, Nanosheet, Niobate, Perovskite, Colloidal Solution

1. INTRODUCTION

Landfilled lead containing products cause increased risk of contamination to the environment such as groundwater. Therefore, many lead-free ferroelectric materials have been extensively investigated. Potassium niobate, KNbO_3 , is a ferroelectric material with an orthorhombic perovskite structure at room temperature. This is one of the most promising candidates for application in lead-free piezoelectric devices because of its large electromechanical coupling constant [1, 2]. However, the application of KNbO_3 ceramic sample has been limited by the poor sinterability using conventional sintering technique. Traditional solid state reaction leads to the grain growth of KNbO_3 powder, which decreased the driving force for the densification of ceramic sample.

Recently we developed simple and unique solution process for fabricating submicron KNbO_3 powders with good sinterability [3-8]. Rock-salt type KF block in a Ruddlesden-Popper type layered perovskite, $\text{K}_2\text{NbO}_3\text{F}$, can be selectively dissolved in water to produce niobate nano-sheets. Subsequent self-assembly process among the nano-sheets in a colloidal solution could yield nanosized KNbO_3 particles at room temperature. The aim of this work is to illustrate the reaction mechanism of the new colloid chemistry method by investigating the environment of Nb atom. Detailed structural informations around the Nb atoms in the nano-sheets and nano-particles have been studied by a combination of a Rietveld refinement using neutron powder diffraction pattern and Nb K-edge XAFS measurements.

2. EXPERIMENTAL

The precursor $\text{K}_2\text{NbO}_3\text{F}$ powders used in this study were synthesized by conventional solid state reaction. High-purity powders with a ratio of $\text{KF} : \text{K}_2\text{CO}_3 : \text{Nb}_2\text{O}_5 = 2.6 : 1 : 1$ were used as starting materials. Calcinations were carried out for the mixed powders in air at 1063 K for 1 h. The synthesized samples were characterized by an electron probe microanalysis (EPMA), X-ray fluorescence spectroscopy (XRF) and powder X-ray diffraction (XRD) analysis.

1 g $\text{K}_2\text{NbO}_3\text{F}$ powders suspended in 100 g of water was stirred over night with magnet stirrer at room temperature. With elapse of time, a white color of suspended solution changed to a clear white solution. This solution was filtered using a membrane filter (pore size, 450 nm) to remove a small amount of coarse grain. An observation of the Tyndall effect indicated that the filtered solution is a colloidal solution consisting of many fine particles suspended in water. As-prepared solutions were stable for 1 year without any precipitation. Nano particles were isolated from colloidal solution using centrifugal separator and air-dried.

Nb K-edge XAFS (XANES/EXAFS) spectra were recorded at room temperature in a transmission mode at BL-10B in KEK-PF with a Si(311) monochromator (ring energy 2.5 GeV and stored current of 250-350 mA). The X-ray was detected ion chambers with N_2 (50%) / Ar (50%) mixed gas and Ar gas for I_0 and I detectors, respectively. Normalization of XANES and data reduction and curve-fitting analysis of EXAFS were

carried out as described elsewhere [9]. The powder neutron diffraction data for structural analysis were collected using a Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES, of Institute for Materials Research (IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai [10]. An incident neutron wavelength λ was 0.18207(7) nm. The fine powder sample was enclosed in a cylindrical vanadium vessel. The data were collected on thoroughly ground powders by a multi-scanning mode in the 2θ range from 3° to 153° with a step width of 0.1° . Rietveld structure refinement was carried out with the program RIETAN2000 [11].

3. RESULTS AND DISCUSSION

The colloidal particles were examined by the observation of the Tyndall effect for the filtered solution. An existence of nano-sheets in the colloidal solution was also identified by a direct TEM observation [6-8]. These experiments indicate that layered oxyfluoride, K_2NbO_3F , is exfoliated into single layers in water at room temperature without an intercalation of bulky bases such as tetrabutylammonium [12].

Figure 1 shows the X-ray absorption near-edge structures (XANES) around Nb K-edge for the samples. The XANES feature is known to be sensitive to the local structure. The XANES spectra of $KNbO_3$ ((b) air-dried sample) and $KNbO_3$ ((c) annealed colloid chemistry sample at 1273 K) are very close to that of $KNbO_3$ ((d) reference sample synthesized by the solid state reaction), exhibiting well-resolved two maxima, while these two maxima are not clearly resolved for $KNbO_3$ colloid. This indicates that the local structure of $KNbO_3$ (b) and $KNbO_3$ (c) are very close to $KNbO_3$ (d), while structure of Nb-O polyhedra in colloidal solution is different from that of bulk Nb-O. The pre-edge peak (at around 18990 eV) found at low energy side of the edge absorption is due to dipole-forbidden transition $1s \rightarrow 3d$. It is generally accepted that the intensity of the pre-edge peak increases as the symmetry around absorbing atom is distorted from the regular octahedron [13]. The pre-edge peak of $KNbO_3$ colloid is more intense than $KNbO_3$ ((d) reference sample). This implies that Nb in $KNbO_3$ colloidal solution is more distorted than NbO_6 octahedra in $KNbO_3$.

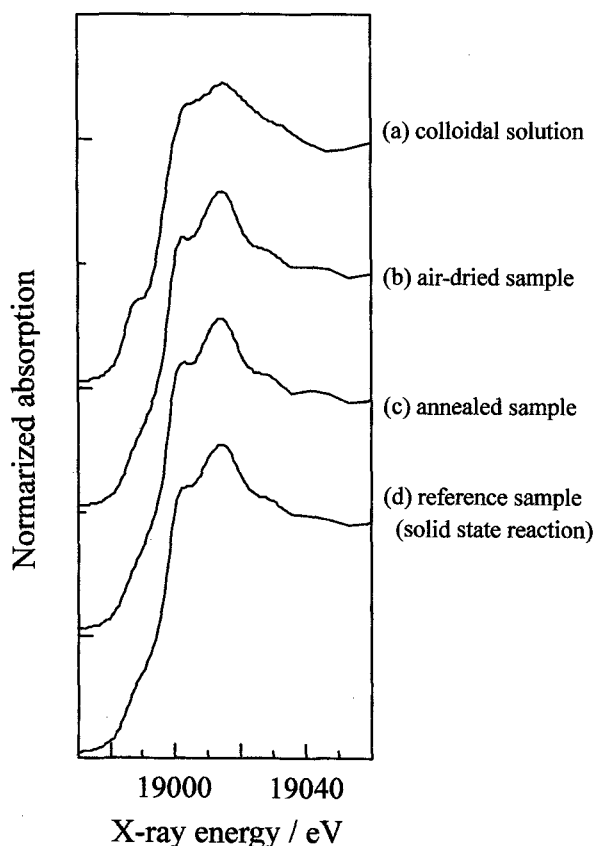


Fig. 1 X-ray absorption near-edge structures (XANES) around Nb K-edge for the samples.

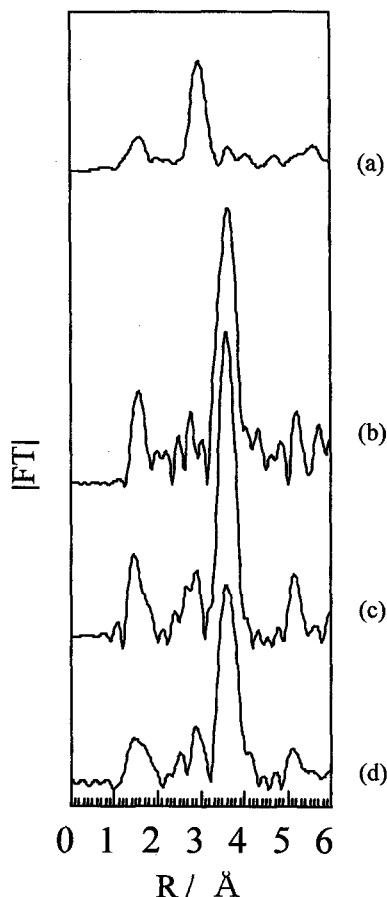


Fig. 2 Fourier transformed spectra of k^3 -weighted EXAFS.

Figure 2 shows the Fourier transformed spectra of k^3 -weighted EXAFS. Peaks in the region 1-2 Å are due to the backscattering by the adjacent oxygen atoms. For KNbO_3 , peaks at 3.0 and 3.6 Å should be due to the backscattering by the neighboring K and Nb atoms, respectively. The EXAFS spectra of KNbO_3 (b) and KNbO_3 (c) are very close to that of KNbO_3 ((d) reference sample). The XANES and EXAFS characterizations show that well-crystallized potassium niobate, KNbO_3 , was synthesized by colloid chemistry method at room temperature. In the EXAFS spectra of the KNbO_3 colloid a peak due to adjacent oxygen (1-2 Å) and a peak at 3.0 Å were observed. The latter peak can be assigned to

neighboring Nb atom. The curve-fitting analysis for the second shell was performed by employing empirical interatomic distance and the coordination number for the KNbO_3 colloidal solution were 3.380 Å and 3.1, respectively. These values are lower than those of KNbO_3 (mean Nb-Nb distance 4.02 Å and coordination number 6). Therefore, the XAFS data suggested that the niobate nano-sheets lost apical fluorine anions in the colloidal solution [14].

Figure 3 shows the powder neutron diffraction pattern fitting for KNbO_3 prepared by the colloid chemistry method. All of the reflections can be indexed with those of the orthorhombic symmetry. The crystallographic data

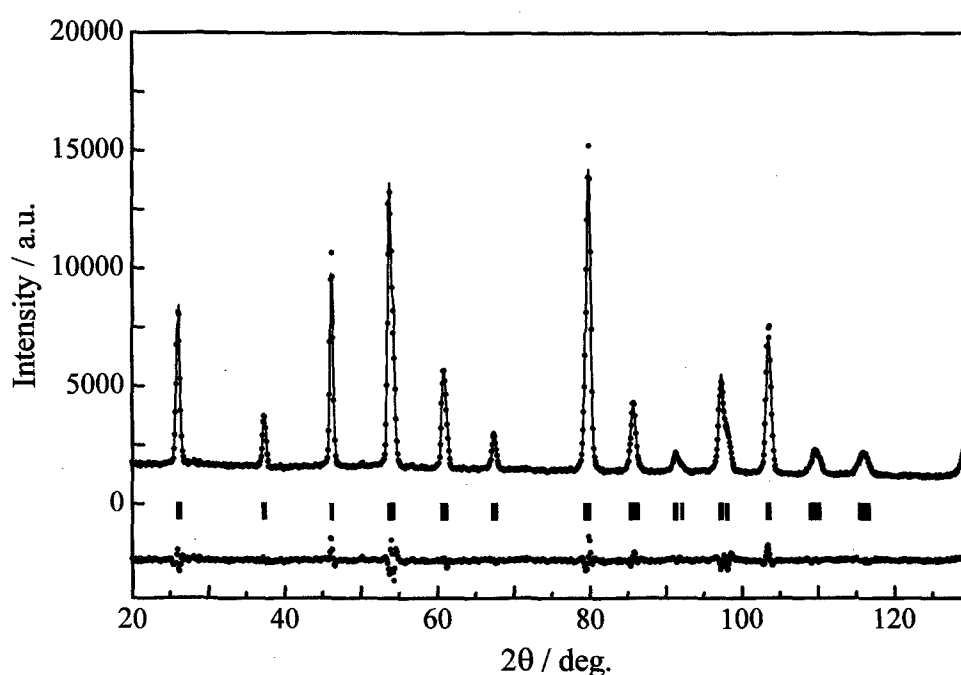


Fig. 3 Rietveld refinement of KNbO_3 (colloid chemistry method) using powder neutron diffraction pattern. The calculated and observed patterns are shown on the top by the solid line and dots, respectively. The vertical marks in the middle show the positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between the calculated and observed intensities.

Table I. Structural parameters and reliable factors of soft chemical KNbO_3 .

Atom	Site	x	y	z	$B_{\text{eq}}(\times 10^{-2}\text{nm}^2)$
K	2a	0.5	0	0.491(4)	0.7(1)
Nb	2b	0	0	0	0.7(1)
O(1)	2a	0.5	0	0.967(2)	0.4(1)
O(2)	4e	0	0.249(1)	0.720(1)	0.7(1)
Lattice parameters (nm)		: $a = 0.39891(3)$, $b = 0.56949(7)$, $c = 0.56968(7)$			
Reliable factors		: $R_{\text{wp}} = 3.86\%$, $R_p = 2.95\%$, $R_e = 2.24\%$, $R_I = 2.09\%$, $R_F = 1.23\%$			
		Goodness of fit $S = 1.72$			

are shown in Table I. The Rietveld refinement using the neutron powder diffraction pattern indicates that the crystal structure of the sample synthesized by the colloid chemistry method essentially maintained the orthorhombic symmetry. This agrees with the results of Nb K-edge XAFS (XANES/EXAFS) spectra. However, the orthorhombic distortion for the colloid chemistry sample was smaller than that of solid state reaction sample [15]. The origin of their crystallographic behavior is unclear at present.

The XANES and EXAFS data demonstrate that the observed restructuring process from two-dimensional to three-dimensional perovskite was explained by the exfoliation-restacking mechanism. When a layered perovskite precursor, K_2NbO_3F , is immersed in water, the rock-salt-type block, KF, is selectively dissolved in water and the exfoliations into nano-sheets can occur. The restacking of the exfoliated rigid 2D nano-sheets into 3D perovskite is progressing rapidly in the centrifugation process. This colloid chemistry route using the selective dissolution of the layered perovskite precursors is a powerful tool for the low-temperature preparation of the nano-particles and thin films.

4. CONCLUSIONS

The reaction mechanism of new colloid chemistry method for the preparation of well-crystalline $KNbO_3$ nano-particles were investigated by Nb K-edge XAFS (XANES/EXAFS) spectroscopy. The exfoliation - restacking mechanism for restructuring of perovskite nanosheets can explain the observed colloid chemical reaction. This technique is a typical build-up process and could make a contribution to the development of atomic-scale synthetic technology in the field of the nanotechnology.

ACKNOWLEDGMENT

This work was supported by the "Research for the Future, Preparation and Application of Newly Designed Solid Electrolytes (JSPS RFTF96P00102)" program from the Japan Society for the Promotion of Science (JSPS).

REFERENCES

- [1] K. Yamanouchi, H. Odagawa, T. Kojima and T. Matsumura, *Electronic Letters*, **33**, 193 (1997).
- [2] K. Nakamura and Y. Kawamura, *IEEE Trans. Ultrason. Ferroelect. Freq. Contr.*, **47**, 750-55 (2000).
- [3] F. Galasso and W. Darby, *J. Phys. Chem.*, **66**, 1318-20 (1962).
- [4] K. Toda, N. Sakai, H. Ohnuma, Y. Aoyama, S. Tokuoka, M. Sato, *Ext. Abstr. (The 25th Symposium on Solid State Ionics in Japan 1999)*; *The Solid State Ionics Society of Japan*, 2A9.
- [5] S. Tokuoka, K. Toda, K. Uematsu and M. Sato, *Ext. Abstr. (Spring Meet. 2000)*; *The Ceramic Society of Japan*, 1122.
- [6] K. Toda, S. Tokuoka, K. Uematsu and M. Sato, *Key Eng. Mater.*, **214-215**, 67-74 (2002).
- [7] K. Toda, N. Ohtake, M. Kawakami, S. Tokuoka, K. Uematsu and M. Sato, *Jpn. J. Appl. Phys.*, **41**, 7021-24 (2002).
- [8] K. Toda, S. Tokuoka, N. Ohtake, K. Uematsu and M. Sato, *Key Eng. Mater.*, **248**, 27-30 (2003).
- [9] K. Nishi, K. Shimizu, M. Takamatsu, H. Yoshida, A. Satsuma, T. Tanaka, S. Yoshida and T. Hattori, *J. Phys. Chem. B*, **102**, 10190-95 (1998).
- [10] K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, Y. Yamaguchi, *Jpn. J. Appl. Phys.*, **37**, 3319-26 (1998).
- [11] F. Izumi and T. Ikeda, *Mater. Sci. Forum*, **321-324**, 198-203 (2000).
- [12] M. Fang, C. H. Kim, A. C. Sutorik, D. M. Kaschak and T. E. Mallouk, *Mat. Res. Soc. Symp. Proc.* **446**, 377-82 (1997).
- [13] S. Yoshida, T. Tanaka, H. Yoshida, T. Hanada, T. Hiraiwa, H. Kanai and T. Funabiki, *Catal. Lett.*, **12**, 277 (1992).
- [14] L-S. Du, F. Wang and C. P. Grey, *J. Solid State Chem.*, **66**, 285-94 (1998).
- [15] A. W. Hewat, *J. Phys. C*, **6**, 2559-72 (1973).

(Received October 11, 2003; Accepted March 17, 2004)